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Molecular-dynamics simulations of SiH_3 radical deposition on hydrogen-terminated silicon (100) surfaces

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We have performed molecular-dynamics simulations using realistic many-body semiclassical potentials for hydrosilicon interactions to investigate the deposition and diffusion dynamics of thermal to hyperthermal SiH_3 radicals on hydrogen-terminated silicon (100) surfaces. We have studied the radical diffusion length as a function of different incident radical energies to know the effect of the radical energization on the radical diffusion upon a substrate. As a result of the deposition and diffusion dynamics simulation using 100 radicals, it was observed that when radicals having an incident kinetic energy of about 700 K adsorb vertically on a substrate with high hydrogen coverage, the average diffusion length is the largest and the value is about 32 Å. It was found that the incident energized radical has an optimum energy to maximize the radical diffusion length on a substrate under some conditions.

I. INTRODUCTION

Thin films of hydrogenated amorphous silicon (*a*-Si:H) fabricated by plasma-enhanced chemical vapor deposition[1] (PECVD) are valuable for functional materials used in electronic devices such as solar cells.[2] The structural, electrical, and optical properties of *a*-Si:H greatly depend on some manufacturing conditions in PECVD. Thus it is very important to understand the surface processes of film growth microscopically to control the structure of *a*-Si:H films. Current experimental measurements, however, are insufficient to understand these processes. Thus process simulations with computers have been used in recent years.

Some Monte Carlo simulations[3,4] of hydrogenated amorphous silicon thin-film growth have been carried out to comprehend those processes. But the Monte Carlo method needs many assumptions and a lot of parameters, and often loses physical meanings.[5] On the other hand, the molecular-dynamics method is an important tool for understanding atomic-scale chemical processes. Central to the success of this type of study is the incorporation of an interatomic potential-energy expression which can accurately describe chemical bonding. Tersoff has introduced a relatively simple many-body expression which accurately describes the bonding in various silicon polymorphs.[6] In addition, it is reported that Tersoff-type potentials would be especially useful for applications in materials science, where many processes fall at the interface of gas-phase and solid-phase chemistry.[7]

In a previous study, we have confirmed that the Tersoff potentials for Si are suitable for *a*-Si formation,[8] and have developed Tersoff-type potentials[9] suitable for *a*-Si:H formation by rapid quenching. In addition, we have been recently applying a molecular-dynamics method with the Tersoff-type potentials to analyses of *a*-Si:H thin-film growth processes. From previous experimental results by others,[10] it has been found that SiH_3, SiH_2, and the H radical can have an influence on these processes and that, in particular, the SiH_3 radical is a significant precursor.[11] In addition, an experimental method has been recently reported in which the defect density in *a*-Si:H deposited at low substrate temperatures decreased with addition of thermally energized growth precursors by a heated mesh in a plasma-enhanced chemical vapor deposition apparatus.[12] In this work, we have performed molecular-dynamics simulations of deposition and diffusion dynamics of 100 SiH_3 radicals on hydrogen-terminated silicon (100) surfaces with the initial position randomly chosen and the initial energy constant, and have investigated the average radical diffusion length as a function of different incident radical energies. Hydrogen-terminated crystalline silicon was used as the substrate. The methodology in the molecular-dynamics simulations is mentioned in the following Sec. II. In Sec. III, the results of the simulations are presented and discussed. Finally, Sec. IV summarizes the conclusions to be drawn from this work.

II. THEORETICAL METHODS

In this work we employ an empirical many-body potential which realistically describes bonding in hydrosilicon systems and assumes the form[9]

$$U=\sum_i \sum_{j>i} [A_{ij} V_r(r_{ij}) - B_{ij} V_a(r_{ij})] , \quad (1)$$

where V_r and V_a are terms which represent pair-repulsive and pair-attractive interactions, respectively, while A_{ij} and B_{ij} are many-body bond-order terms which depend on the atomic coordination and angles. This potential is based on a Tersoff bond-order expression[6] and predicts *a*-Si:H structure and SiH_3 radical structure.[9]

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In order to model a (100) silicon surface, we utilize a slab of eight layers of silicon atoms having 32 atoms per layer with the (100) face exposed reconstructed into a (2×1) dimerized surface and terminated by hydrogen atoms. The bottom two layers are held rigid in their equilibrium position while the remaining layers are allowed to move with full dynamics. The substrate temperature is maintained by immersing the silicon atoms on the third, fourth, and fifth layers from the bottom in a thermostat employing the velocity scaling method of Berendsen *et al.*[13] Periodic boundary conditions were employed in the two directions parallel to the surface. A hydrogen atom was removed from the fully hydrogen-terminated surface to model a 50% hydrogen-covered surface.

The simulation is initiated by equilibrating the substrate to a desired temperature. A SiH_3 radical with incident center-of-mass energy E and incident angle θ is allowed to collide with the surfaces. The initial position of the center of mass of the incident radical is chosen from the random sets of coordinates in the plane of the surface and then moved away from the surface such that the radical experiences no initial interaction with the substrate. The trajectories of all the particles are determined by integrating the equations of motion according to the velocity form of the Verlet algorithm.[14] The typical time step employed in the simulations is 0.1 fs, and the total simulation time is 3.0 ps.

III. RESULTS AND DISCUSSION

A. Si(100)-2×1:H surface

First we have studied the Si(100)-2×1 structure by performing molecular-dynamics simulations with our Tersoff-type potential[9] mentioned in Sec. II. Initially, all the atoms were placed in a structure corresponding to a perfect crystal, and the energy was calculated; this gives the energy of a perfect unreconstructed surface. Then the structure was distorted toward that of the 2×1 dimer reconstruction. The system adopted a 2×1 dimer structure, which is a local minimum (and most likely the global minimum) on the potential surface for the system. The reconstructed surface had an energy that was 2.04 eV/dimer lower than that of the perfect unreconstructed surface. We have summarized the results on the relaxation energy and the separation of the dimers, and compared with a measured value obtained by scanning tunneling microscopy[15] (STM) and other models in Table I. Our results are similar to those of the density-functional theory in the local-density approximation (DFT-LDA) and of all the other potential functions tested, and the measured value.

Next we have studied the Si(100)-2×1:H structure by performing molecular-dynamics simulations. Initially, all the silicon atoms were placed in a structure corresponding to a perfect crystal and a monolayer of hydrogen atoms was put above the surface silicon atoms. Then the structure was distorted toward the Si(100)-2×1:H structure. It was observed that hydrogen atoms open outward on the Si dimers. This result corresponds to the prediction by STM (Ref. 21) and low-energy electron-diffraction[22] (LEED) experiments. We have summarized the results on the separation of the Si dimers, Si-H bond length, and H-Si-Si bond angle, and compared them with other models in Table II. Our results are almost equal to those of a "large cell" in the shape of a slab modified intermediate neglect of differential overlap[23] (SLAB-MINDO) and the other potential function tested.[24] In addition, our potential predicts energies of −0.50 and −0.91 eV/(surface atom) for the hydrogen-covered bulk-terminated Si(100) surface and hydrogen-covered Si(100)-2×1 reconstruction, respectively, relative to the clean Si(100)-2×1 reconstruction plus gas-phase H_2 molecules. From this result, it was found that the clean Si(100)-2×1 reconstructed surface is easily covered by hydrogen atoms.

TABLE I. Si(100)-2×1 dimer reconstruction. The relaxation energy per dimer reported here is the energy of the perfect unreconstructed surface minus the energy of the 2×1 structure, divided by the number of dimers. R_{dimer} is the separation of the dimers in the equilibrium structure. "Expt. " shows an experimental value by STM measurement. The Yin and Cohen (YC) and Pandey references are density-functional calculations. The Stillinger and Weber (SW), Biswas and Hamann (BH), Bolding and present values are molecular-dynamics simulations with semiempirical potentials

Method	R_{dimer} (Å)	Relaxation energy per dimer (eV/dimer)
Expt. (STM, Ref. 15)	2.40	
YC (Ref. 16)	2.25	1.70
Pandey (Ref. 17)	2.22	2.06
SW (Ref. 18)	2.41	1.68
BH (Ref. 19)	2.42	1.73
Bolding (Ref. 20)	2.36	1.60
Present	2.37	2.04

These results showed that our potentials[9] are suitable for the Si(100)-2×1 and Si(100)-2×1:H structures. The details of molecular-dynamics (MD) simulations of SiH_3 radical deposition on the Si(100)-2×1:H surface are presented in the following subsection.

B. SiH_3 diffusion length on a substrate

First it was confirmed that the SiH_3 radical adsorbs and diffuses on the hydrogen-terminated substrate in our MD simulations. Then we calculated the radical diffusion lengths for 100 radicals having the same incident angle θ and energy E with the initial position randomly chosen. The angle was set at 90° and 45°, and the energy at 0.03, 0.06, 0.1, and 0.5 eV. In this study, we assume that the incident center-of-mass kinetic energies E of the energized radicals[25] are increased by a heated mesh.[26] As a result of MD simulations, we observed that all of the 100 SiH_3 radicals adsorb and diffuse with several bounces, and finally stay on the substrate. None of the radicals was seen to escape from the surface. The simulated results for average diffusion lengths are shown

TABLE II. Si(100)-2×1:H surface reconstruction. The MINDO and classical MD references are a periodic SLAB-MINDO calculation and a molecular-dynamics simulation with semiempirical potentials, respectively. The Si-Si, Si-H, and θ(H-Si-Si) show the separation of the Si dimers, the Si-H bond length, and the H-Si-Si bond angle, respectively.

Method	Si-Si (Å)	Si-H (Å)	θ(H-Si-Si) deg
MINDO (Ref. 23)	2.42	1.533	110.2
Classical MD (Ref. 24)	2.43	1.580	112.4
Present	2.40	1.521	111.9

in Figs. 1 and 2, respectively, where Γ denotes hydrogen coverage. In this case Γ is 100%, which means that all the surface silicon atoms are covered with a monolayer of hydrogen. The radical diffusion length is obtained by calculating the diffusion length of the Si atom of SiH_3 and averaging the results for 100 SiH_3 radicals. The number of radicals was adequate to make the average value valid. In these figures the error bars denote a region including 100 values. From Fig. 1, it is seen that, when radicals having an incident kinetic energy of about 0.06 eV adsorb vertically on a substrate, the average radical diffusion length is largest and the value is about 32 Å. On the other hand, from Fig. 2, it is found that the radical diffusion length increases when radicals having an incident kinetic energy of more than 0.1 eV adsorb obliquely on a substrate.

The time evolution of the kinetic energy for some of the 100 radicals was analyzed in the case of $E=0.06$ eV (700 K) and $E=0.5$ eV (5830 K) in order to study the reason for the difference in the dependency of the incident kinetic energy on the diffusion length between $\theta=90°$ and 45°. Figure 3 shows the time evolution of one typical radical kinetic energy. Basically the other observed radicals have almost the same time evolution of the kinetic energy as shown in Fig. 3. The top and bottom panels in Fig. 3 correspond to the results for $\theta=90°$ and 45°, respectively, obtained during the initial 500 fs. The time of the collision between an incident radical and the substrate is 192 fs ($E=0.06$ eV) and 96 fs ($E=0.50$ eV) for $\theta=90°$, and 232 fs ($E=0.06$ eV) and 142 fs ($E=0.50$ eV) for $\theta=45°$. From the top panel, it can be seen that the kinetic energy of an incident radical with a low energy of 0.06 eV gets higher temporarily in the case of $\theta=90°$, while the energy of a radical with a high energy of 0.50 eV gets lower in the same case. It could be thought that the former energy gain is due to the interaction between the incident radical and a hydrogen atom on the substrate, and that the latter energy loss is due to a strong collision between the incident radical and the substrate. This time evolution of the radical kinetic energy for $\theta=90°$ supports the result that the diffusion length is larger for low incident kinetic energy and smaller for high incident kinetic energy, indicated for $\theta=90°$ in Fig. 1.

On the other hand, from the bottom panel in Fig. 3, it can be seen that the kinetic energy of an incident radical with low energy of 0.06 eV stays low in the case of $\theta=45°$, and the energy of a radical with high energy of 0.50 eV is kept high in the same case. It could be thought that one of the reasons is that it is hard to lose

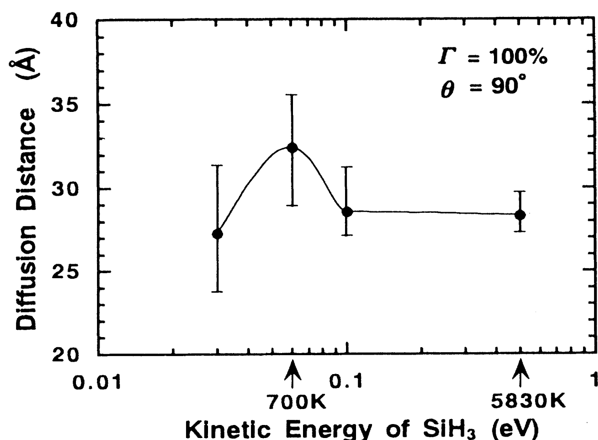

FIG. 1. The average SiH_3 radical diffusion length on a substrate for various incident kinetic energies and an incident angle of 90°. The radical kinetic energy is expressed as center-of-mass kinetic energy. Γ denotes hydrogen coverage, and in this case Γ is 100%, which means that all the surface silicon atoms are covered with a monolayer of hydrogen. The radical diffusion length is obtained by calculating the diffusion length of the Si atom of SiH_3. The error bars show maximum and minimum values of 100 radicals.

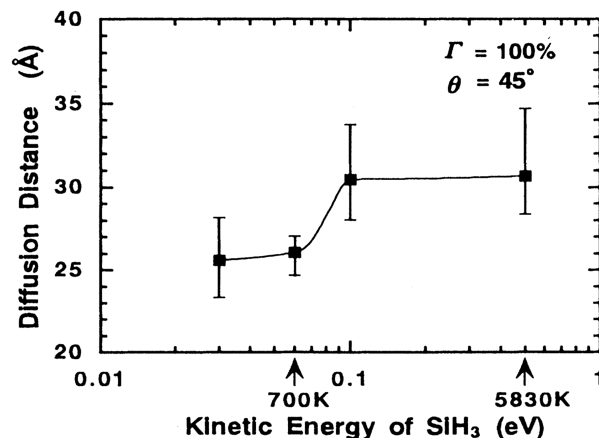

FIG. 2. The average SiH_3 radical diffusion length on a substrate for various incident kinetic energies and an incident angle of 45°.

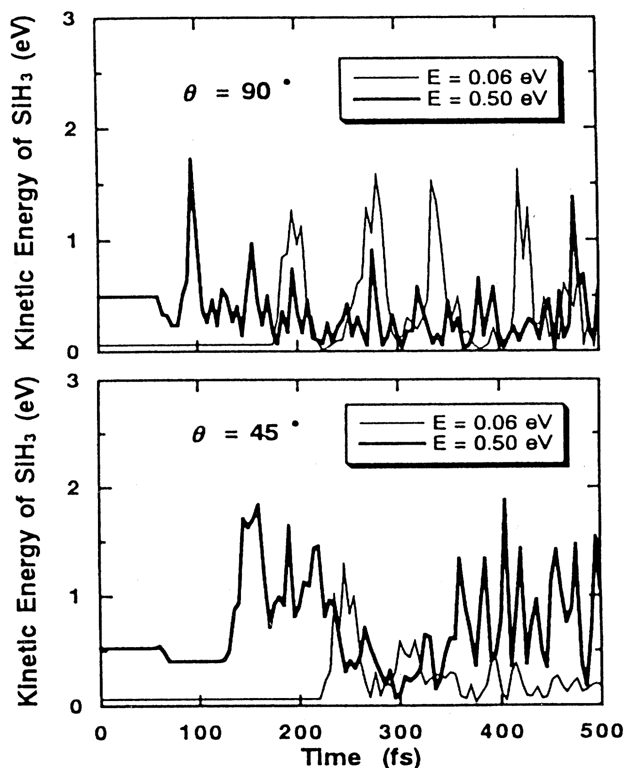

FIG. 3. Time evolution of the kinetic energy of the SiH_3 radical for an adsorption event. Top and bottom panels correspond to the results for $\theta=90°$ and 45°, respectively, and are obtained during the initial 50 fs. The time of the collision between the incident radical and the substrate is 192 fs ($E=0.06$ eV) and 96 fs ($e=0.50$ eV)for $\theta=90°$, and 232 fs ($E=0.06$ eV), and 142 fs ($E=0.50$ eV) for $\theta=45°$.

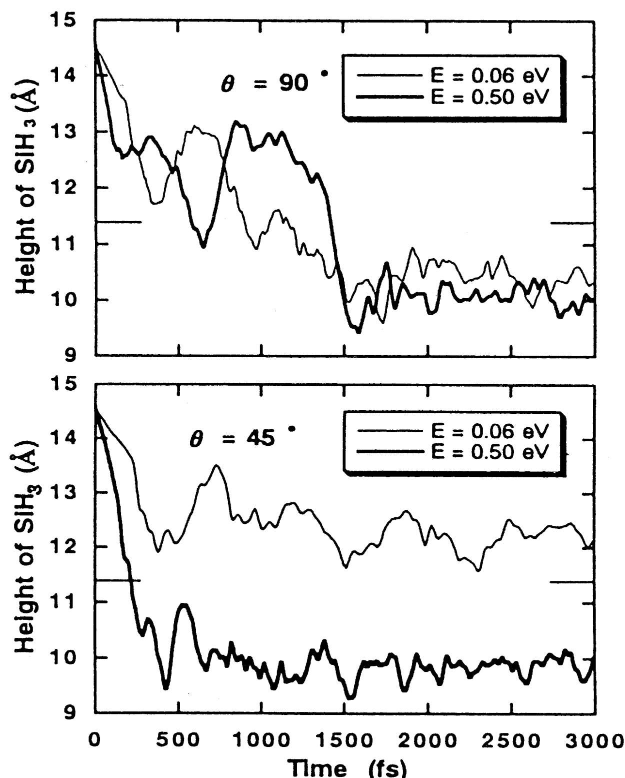

FIG. 4. Time evolution of the height of the SiH_3 radical for an adsorption event. Top and bottom panels correspond to the results for $\theta=90°$ and 45°, respectively, and are obtained during 3000 fs. The height of the top surface is ≈ 11.4 Å and is denoted as the horizontal short solid lines.

the radical momentum parallel to the substrate; namely, the radical energies are almost conserved in the case of $\theta=45°$. That is why the diffusion lengths for the incident radicals having high kinetic energy increase as shown in Fig. 2.

Next, we have studied why the vertically incident radicals with high energies lose energy. One of the reasons could be the collisions between the incident radicals and the substrate. So the phenomena of the collisions have been investigated. Figure 4 shows the time evolution of the z coordinate of SiH_3 in the z axis for one typical SiH_3 radical. Basically the time evolution of the height for the other observed radicals is almost similar to the result in Fig. 4. The top and bottom panels in Fig. 4 correspond to the results for $\theta=90°$ and 45°, respectively, which are obtained during 3000 fs. From the top panel in Fig. 4, it can be seen that a vertically incident SiH_3 radical with the high energy of 0.50 eV collides with the substrate strongly and bounces several times against the substrate, and then gets into the surface. On the other hand, from the bottom panel in Fig. 4, we find that an obliquely incident SiH_3 radical with high energy bounces a little against the substrate and gets into the surface. These results predict that the kinetic-energy loss of a vertically incident radical with high kinetic energy is due to the strong collision between the incident radical and the substrate. All the results mentioned above make it possible

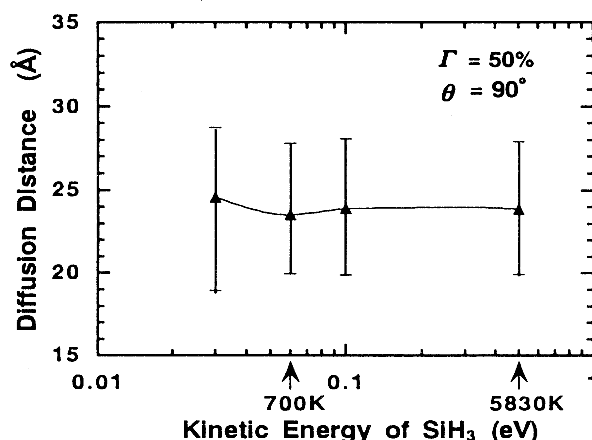

FIG. 5. The average SiH_3 radical diffusion length on a substrate for various incident kinetic energies and a hydrogen coverage of 50%. The incident angle θ is set at 90° in this simulation.

to presume that vertically incident SiH_3 deposition on the substrate is like chemical vapor deposition when the incident kinetic energy is about 0.06 eV (700 K), and that the deposition is like physical vapor deposition when the incident kinetic energy is about 0.5 eV (5830 K).

Finally, we have studied the effect of hydrogen coverage Γ on the SiH_3 radical diffusion length upon a substrate. Figure 5 shows the average diffusion length as a function of different incident kinetic energies for $\Gamma=50\%$. It is found that no dependency of the incident kinetic energy on the radical diffusion length can be seen in the case of $\Gamma=50\%$, and that the average radical diffusion length for $\Gamma=50\%$ is about 5 Å less than that for $\Gamma=100\%$ as shown in Fig. 1. In this case the dangling bonds of the surface Si atoms increase because the hydrogen coverage decreases. The SiH_3 radical connects strongly with the dangling bonds of Si. So, whether the kinetic energy of the incident radical is low or high, the radical connects easily with the dangling bonds of surface Si atoms near the site where the radical absorbs on the substrate first. Thus no dependency of the incident kinetic energy on the diffusion length can be seen in this case.

From all the results in this study, we found that the values of the diffusion lengths are from 15 to 35 Å. They correspond to a measured value of tens of angstroms in an estimation by ellipsometry measurement.[27]

IV. CONCLUSIONS

The molecular-dynamics simulations described in this paper represent the individual deposition and diffusion dynamics of thermal to hyperthermal SiH_3 radicals on hydrogen-terminated silicon (100) surfaces. The radical diffusion length as a function of different incident radical energies has been studied to know the effect of the radical energization on the radical diffusion upon a substrate. It was observed under our MD simulation model and some conditions mentioned in this paper that, when radicals having incident kinetic energies of about 700 K adsorb vertically on a substrate with high hydrogen coverage, the average diffusion length is the largest and the value is about 32 Å. It was found that a vertically incident energized radical has the optimum energy to maximize the radical diffusion length on a substrate. The method of generation of strong gas flow toward a substrate in a real experiment can be suggested for the increase of vertically incident radicals on a substrate.

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